Surface characterization of palladium–copper bimetallic catalysts by FTIR spectroscopy and test reactions

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Different bi-metallic palladium–copper catalysts have been prepared according to different sequences of impregnation of a commercial alumina. CO adsorption followed by FTIR spectroscopy was performed in order to identify the nature of the superficial sites. Two test reactions were also used to characterize the nature of the active surface site: gas phase toluene hydrogenation was selected in order to show the hydrogenating activity of metallic palladium, whereas the reaction of decomposition of ethanol, which exhibits 100% selectivity in the formation of ethanal on pure copper catalysts, was also studied on this series of catalysts. The results obtained by both methods are complementary. By comparison with the behaviour of pure palladium or copper based catalysts, they allow to propose hypotheses on the surface composition: separated phases, alloys or a phase covered by the other one.

Keywords: Pd–Cu bimetallics; CO adsorption; FTIR; toluene hydrogenation; ethanol decomposition

1. Introduction

In the characterization of bi-metallic catalysts it is very often difficult to determine the nature of the active surface: more or less separated phases, alloys or one of the phases being coated or partially covered by the other one. The catalytic activity is perhaps the most sensitive response to the surface composition and well chosen sets of test reactions may provide useful information. In the case of palladium–copper systems, the palladium is active toward toluene hydrogenation [1], whereas copper is not active at all. It was also shown that for benzene hydrogenation the turnover frequency decreases with the copper content and that benzene hydrogenation requires an ensemble of three surface palladium atoms [2]. Toluene and benzene hydrogenations appear to be similar reactions [1] and toluene hydrogenation

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was already used to help the characterization of platinum–copper systems [3]. On pure copper based catalysts, the selectivity for ethanol conversion in ethanal is 100% and is clearly related to the metallic copper phase [4,5]. These two reactions were therefore selected in an attempt to characterize a series of palladium–copper catalysts, each preparation being liable to lead to a different surface composition. In addition, FTIR spectroscopy of adsorbed CO is a very useful tool for the identification of the nature of the sites present at the surface of the catalysts.

2. Experimental

2.1. CATALYSTS PREPARATION

An alumina (Oxyd C from Degussa) of specific area of 100 $m^2\ g^{-1}$ has been used as catalyst carrier. Palladium acetylacetonate and copper nitrate have been generally selected as precursors for the preparation of bi- and monometallic samples. Copper acetylacetonate was used for the preparation of the co-impregnated sample. Acetylacetonates were used in benzene solutions, whereas copper nitrate was used in aqueous solutions. After alumina impregnation both solvents were eliminated under vacuum in a rotating evaporator. The resulting materials were dried in an oven for 3 h at 110°C. Two monometallic catalysts Pd/Al_2O_3 and Cu/Al_2O_3 were prepared as references.

Different sequences of impregnation were used for the preparation of the bimetallic catalysts. Two of the preparations were aimed at investigating the effect of the order of deposition of the metallic phases:

– impregnation by palladium acetylacetonate in benzene solution, drying in an oven at 110°C, followed immediately by copper deposition from aqueous nitrate solution. The resulting catalyst is denoted $(Cu + Pd)/Al_2O_3$.

– copper deposition from aqueous nitrate solution, drying in an oven at 110°C, followed immediately by impregnation with palladium acetylacetonate: catalyst referred to as $(Pd + Cu)/Al_2O_3$.

For the third preparation copper was deposited first and the resulting solid calcined for 1 h at 500°C in order to obtain copper oxide, palladium was then introduced using palladium acetylacetonate; the resulting sample is labelled $(Pd/CuO)/Al_2O_3$.

For the fourth preparation, after impregnation with palladium acetylacetonate, the solid is reduced for 1 h in hydrogen at 500°C to give metallic palladium. Copper is then deposited from copper nitrate solution leading to the sample labelled $(Cu/Pd)/Al_2O_3$.

The last preparation consists in a co-impregnation from a solution of copper and palladium acetylacetonates; the resulting catalyst is labelled $(Pd, Cu)/Al_2O_3$.

All the prepared samples were finally calcined under oxygen for 1 h at 500°C, then reduced for 5 h under flowing hydrogen at the same temperature. XRD patterns evidenced only peaks due to alumina (δ form), no peak assigned to palladium or copper containing phases were detected suggesting the presence of highly dispersed metallic phases. As a matter of fact, after ageing under hydrogen at high temperature (1000°C), big copper–palladium particles have been observed from XRD measurements [6].

2.2. FTIR SPECTROSCOPY

Spectra were recorded on an IFS 110 spectrometer from Bruker in the 4000–1200 cm^{-1} range with a resolution set at 4 cm^{-1}. The background of the reduced sample was used as reference and the plot function was set in absorbance mode. Samples were compressed in order to obtain thin discs of self-supported material (18 mm in diameter, weight between 20 and 35 mg). The discs were introduced in a cell which allowed in situ experiments. The catalysts were reduced again in flowing hydrogen at 500°C overnight and evacuated at the same temperature for 2 h in order to obtain palladium containing particles free of adsorbed hydrogen. Carbon monoxide was introduced at room temperature under a 20 Torr pressure; the resulting samples were first evacuated at room temperature, then at increasing temperature.

2.3. CATALYTIC ACTIVITY MEASUREMENTS

The two reactions are performed in a micro dynamic differential reactor; the conversion is kept below 5%.

An amount of 10 to 40 mg of catalyst is diluted in 100 mg of glass powder and is reduced for 3 h at 500°C in a hydrogen flow (60 cm^3 min^{-1}).

Toluene hydrogenation. The partial pressure of toluene of 17 Torr (2.27 kPa) is completed by hydrogen to atmospheric pressure and the total flow rate is 60 cm^3 min^{-1}. The initial rates of the reaction are measured at 150°C. In the operating conditions the only product of the reaction is methylcyclohexane for palladium containing catalysts, whereas the catalyst containing only copper is not active at all for this reaction.

Ethanol decomposition. The partial pressure of ethanol is 35 Torr (4.67 kPa) in a helium flow; the total pressure is the atmospheric pressure and the total flow rate is 60 cm^3 min^{-1}. The temperature of the reaction is 190°C.

3. Results and discussion

3.1. FTIR MEASUREMENTS OF CO ADSORPTION

3.1.1. Monometallic catalysts

CO irreversibly adsorbed at room temperature on the Pd/Al_2O_3 leads to the appearance of two main νCO bands at 2070 and 1960 cm^{-1} (fig. 1) attributed to

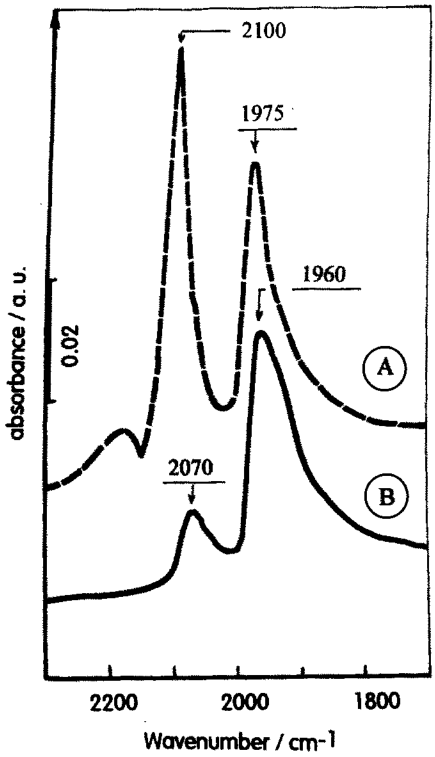

Fig. 1. FTIR spectra of CO adsorbed at room temperature onto a Pd/Al_2O_3 sample: (A) under 10 Torr CO pressure, (B) after evacuation for 30 min at room temperature.

CO bonded to surface palladium atoms in the linear and in the bridged forms respectively [7]. The contribution to the total absorbance of the band due to the linear form was deduced from the ratio $R = A_L/(A_L + A_B)$, A_L and A_B being the integrated absorbance of the 2070 and 1960 cm^{-1} bands normalized to one gram of palladium respectively. The R value must not be considered as the percentage of CO linearly bonded since the extinction coefficients were not determined. The value of R is 0.15, i.e. very close to the value reported in previous works [8]. In addition, the integrated absorbance of the bridged form also normalized to one gram of palladium was found equal to 11×10^4 a.u. Finally, from the global absorbance $A_L + A_B$ and according to a previous calibration [8], the fraction of palladium metallic area accessible to gases (or dispersion) is close to 37%.

By desorption at increasing temperature, the intensity of both bands decreased. They are removed from the IR spectra by desorption between 150 and 200°C. After desorption at 100°C, the two νCO bands were observed at 2060 and 1925 cm^{-1}. The 1925 cm^{-1} band might arise either from the shift of the 1960 cm^{-1} absorption with the decrease in CO coverage or from CO bonded in the bridge form onto palladium belonging to various crystal planes [9].

In the case of the Cu/Al_2O_3 sample, the adsorption of CO at room temperature gives rise to the formation of a main band at 2110 cm^{-1} with a shoulder at 2135 cm^{-1}. The intensities of both bands strongly decrease by desorption at room temperature. They disappear from the IR spectrum after evacuation between 50 and 100°C. According to previous data, adsorption of CO onto metallic copper leads to a single νCO vibration located between 2080 and 2110 cm^{-1} according to the crystal plane and to the nature of the support [7]. The band at ca. 2110 cm^{-1} observed in the present work must be assigned to CO linearly adsorbed onto metallic copper. The shoulder at 2135 cm^{-1} is usually attributed to CO adsorbed onto oxidized copper [10]. According to the conditions of reduction (500°C under hydrogen), the presence of remaining free copper oxides must be ruled out. The formation of small amounts of copper aluminate during the initial calcination under oxygen at 500°C could be at the origin of the 2135 cm^{-1} band.

3.1.2. Bimetallic catalysts

The (Cu + Pd)/Al_2O_3, (Pd + Cu)/Al_2O_3 and (Pd/CuO)/Al_2O_3 bimetallic samples exhibited similar behaviour towards carbon monoxide adsorption. Under a 10 Torr CO pressure at room temperature, IR spectra show the presence of bands (fig. 2) at 2140–2110 cm^{-1} (CO bonded to copper aluminate and metallic copper), 2065 and 1980 cm^{-1} (CO bonded to metallic palladium in the linear and bridge

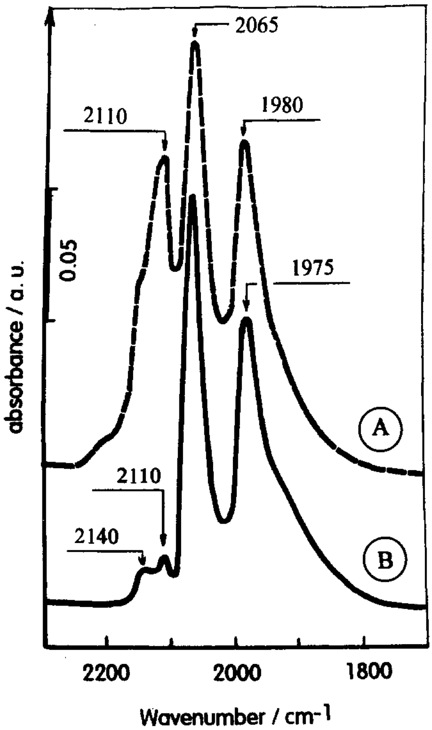

Fig. 2. FTIR spectra of CO adsorbed at room temperature onto a (Cu + Pd)/Al_2O_3 sample: (A) under 10 Torr CO pressure, (B) after evacuation for 30 min at room temperature.

form respectively). After 30 min of evacuation at room temperature, the bands due to CO adsorbed on copper strongly decrease and the bands attributed to CO chemisorbed onto palladium are still present at 2065 cm^{-1} for the linear form and now at 1975 cm^{-1} for the bridged form. Upon vacuum treatments at higher temperatures these bands are progressively eliminated. After desorption at 150°C, they are observed at 2055 and 1920 cm^{-1}, i.e. at wavenumbers very close to the values reported onto pure palladium in the same conditions. By contrast with the Pd/Al_2O_3 sample, the percentage of linear form strongly increases by copper addition. For these three catalysts, the R values are in the 0.34–0.44 range (table 1). The increase in the $A_L/(A_L + A_B)$ values must be connected with the dilution of palladium atom ensembles by copper atoms at the surface of the bimetallic particles. In addition the integrated absorbance of the band due to CO bridge bonded to palladium decreases by copper incorporation (table 1). For the three samples similar values for the integrated absorbance A_B are observed.

In the case of the $(Cu/Pd)/Al_2O_3$ catalyst, the band between 1980 and 1960 cm^{-1} is strongly decreased compared with the three previous catalysts, whereas the positions of the various IR bands are not modified. The percentage of the linear form increases up to 0.6 (table 1) indicating that a greater amount of copper is present at the surface of the palladium particles. As a consequence, the integrated absorbance of the band due to bridge bonded CO decreases to 2.3×10^4 a.u.

For the $(Pd, Cu)/Al_2O_3$ sample, the behaviour of CO adsorption is slightly different. Very strong bands of CO adsorbed onto metallic copper are observed suggesting that large amounts of copper are present at the surface of the catalyst. Nevertheless the $A_L/(A_L + A_B)$ ratio is ca. 0.2, i.e. close to that of pure palladium supported on alumina. In addition, the integrated absorbance of the bridged form of CO is 1.84×10^4 a.u., which is much smaller than the value observed on the monometallic catalysts Pd/Al_2O_3.

Table 1
IR data concerning CO adsorption onto palladium and palladium–copper phases supported onto alumina

Sample	Pd (wt%)	Cu (wt%)	A_B [a]	$A_L/(A_L + A_B)$ [b]
Pd/Al_2O_3	1.68	0	10.8×10^4	0.152
$(Cu + Pd)/Al_2O_3$	1.68	1.87	7.6×10^4	0.40
$(Pd + Cu)/Al_2O_3$	1.69	1.87	7.2×10^4	0.34
$(Pd/CuO)/Al_2O_3$	1.81	2.06	5.5×10^4	0.44
$(Cu/Pd)/Al_2O_3$	2.0	2.5	2.6×10^4	0.60
$(Pd, Cu)/Al_2O_3$	1.7	1.0	1.84×10^4	0.20

[a] A_B: integrated absorbance of the band due to CO bridge bonded to palladium, expressed per gram of palladium.

[b] $A_L/(A_L + A_B)$: percentage of linear form in the spectrum of adsorbed CO. A_L and A_B are the integrated absorbance of the bands due to linear and bridged CO species, respectively.

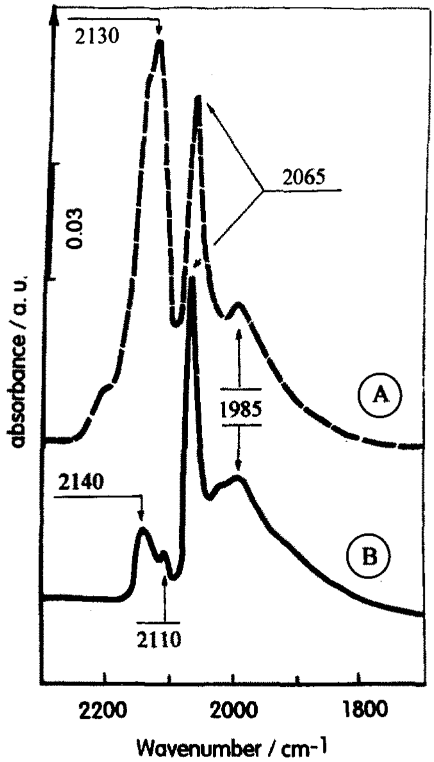

Fig. 3. FTIR spectra of CO adsorbed at room temperature onto a (Cu/Pd)/Al_2O_3 sample: (A) under 10 Torr CO pressure, (B) after evacuation for 30 min at room temperature.

3.1.3. Main conclusions from FTIR measurements

The wavenumbers of CO adsorbed on palladium atoms are very similar for Pd/Al_2O_3 samples with or without copper additive, at full as well as at low coverage. As a matter of fact, the bands due to the CO singleton (at low coverage) are very close and independent of the presence of copper. Such a behaviour suggests the absence of electron transfer between palladium and copper: the electronic properties of palladium atoms are not strongly modified by copper addition.

The proportion of CO linearly bonded increases by copper incorporation, whatever the preparation procedure of the bimetallic sample. In the case of (Cu + Pd)/Al_2O_3, (Pd + Cu)/Al_2O_3 and (Pd/CuO)/Al_2O_3 samples, a dilution of palladium ensembles by copper atoms occurs. At the surface of the metal particles, there is a coexistence of Pd and Cu atoms. Copper addition results in a strong decrease in the amount of palladium atoms able to chemisorb CO in the bridged form.

The behaviour of the (Pd, Cu)/Al_2O_3 catalyst notably differs from that of the other bimetallic samples. Copper appears mainly located at the surface of the metallic particles, whereas palladium particles almost free of copper are observed.

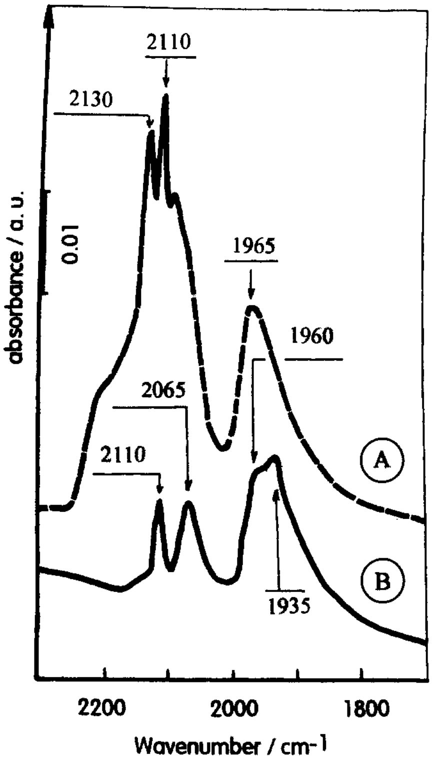

Fig. 4. FTIR spectra of CO adsorbed at room temperature onto a (Pd, Cu)/Al_2O_3 sample: (A) under 10 Torr CO pressure, (B) after evacuation for 30 min at room temperature.

3.2. CATALYTIC ACTIVITY MEASUREMENTS

3.2.1. Monometallic samples

At 150°C, toluene hydrogenation only produces methylcyclohexane over the Pd/Al_2O_3 catalyst. Copper supported on alumina is completely inactive in the same conditions of reaction.

At 190°C, with ethanol, the Cu/Al_2O_3 catalyst shows a selectivity of 100% towards ethanal formation (note that the formation of diethyl ether on the support is not taken into consideration). The Pd/Al_2O_3 catalyst is very active in the conversion of ethanol, in addition significant amounts of methane are also obtained. In this latter case, carbon monoxide is also detected, but its analysis cannot be performed quantitatively because of the presence of methane. For Pd/Al_2O_3, the activity for the formation of methylcyclohexane is 5.4 times the activity for the formation of methane and 0.6 times the activity for the formation of ethanal.

Table 2 shows the initial rates of both reaction expressed in millimoles of reactant converted (into methylcyclohexane or into ethanal) per gram of metal (copper or palladium).

Table 2
Compositions and activities (*a*) of the catalysts

Sample	%Pd	%Cu	*a* toluene[a]	*a* CH_3CHO[b]	*a* CH_4[c]
Pd/Al_2O_3	1.78	0	700	1160	130
Cu/Al_2O_3	0	1.97	0	200	0
$(Cu+Pd)/Al_2O_3$	1.68	1.87	100	420	60
$(Pd+Cu)/Al_2O_3$	1.69	1.87	150	550	67
$(Pd/CuO)/Al_2O_3$	1.81	2.06	160	700	32
$(Cu/Pd)/Al_2O_3$	2.0	2.5	0	310	8
$(Pd, Cu)/Al_2O_3$	1.7	1.0	18	85	4

[a] *a* toluene: toluene hydrogenation at 150°C in mmol (g Pd)$^{-1}$

[b] *a* CH_3CHO: ethanol conversion in ethanal at 190°C in mmol (g (Pd+Cu))$^{-1}$

[c] *a* CH_4: ethanol conversion in methane at 190°C in mmol (g Pd)$^{-1}$.

3.2.2. Bimetallic catalysts

The introduction of copper in the Pd/Al_2O_3 reference sample leads to a decrease in the activity in toluene hydrogenation. In the conversion of ethanol, copper addition decreases the activity in ethanal formation as well as the selectivity into methane.

The initial rates of reactions are expressed in millimoles per gram of palladium for methylcyclohexane formation in toluene hydrogenation and for methane formation in the ethanol decomposition reaction. The rate of production of ethanal (which is produced by copper and by palladium) is reported to the total amount of metallic phase. These activities are given in table 2.

In the two reactions investigated, the activities of $(Cu+Pd)/Al_2O_3$, $(Pd+Cu)/Al_2O_3$ and $(Pd/CuO)/Al_2O_3$ are very similar, the activities in both reactions are very close as well as the ratio of the activities for methylcyclohexane to methane formations: 1.7, 2.2 and 5 respectively. This value, lower than the value obtained for the palladium catalyst, may indicate that palladium and copper are partially alloyed so that the specific activity of the palladium for toluene hydrogenation is decreased and the activity in the formation of ethanal is intermediate between the values observed for Pd/Al_2O_3 and Cu/Al_2O_3. Such a conclusion is in complete agreement with FTIR measurements of CO adsorption, in which the formation of a surface Pd–Cu alloy has been found.

The $(Cu/Pd)/Al_2O_3$ catalyst prepared by deposition of copper from an aqueous solution of copper nitrate onto a Pd/Al_2O_3 sample previously reduced by hydrogen, does not show any measurable activity in toluene hydrogenation and presents only a very small activity for methane formation. Nevertheless, the activity for ethanal formation is on the same order of magnitude as the activity of the Cu/Al_2O_3 catalyst. This observation suggests the presence of a copper phase coating the palladium particles. Indeed infrared measurements have shown that copper addition leads to a weak band due to CO bridge bonded. In comparison with catalytic activity measurements, it appears that isolated palladium atoms, which are only able to chemisorb CO in the linear form, are not active in toluene hydrogenation, as already evidenced in previous works.

The (Pd, Cu) / Al_2O_3 catalyst which is obtained by co-impregnation from acetylacetonate solutions shows a low activity in ethanal formation, whereas its activity in toluene hydrogenation is not suppressed as in the previous sample. Such a behaviour is in agreement with the conclusion deduced from FTIR data: two types of metallic particles are present at the surface of alumina, one type is constituted by palladium particles fully covered by metallic copper, whereas the other one is composed of the remaining palladium phase practically free of copper.

4. Conclusion

The surface properties of palladium–copper bimetallic catalysts are strongly modified according to the procedure of preparation. The surface composition can be followed by the FTIR changes in the spectrum of adsorbed carbon monoxide. Copper introduction leads either to a dilution of the palladium surface atoms or to the covering of the palladium particles by copper atoms. As a consequence, the catalytic properties are deeply modified in agreement with the conclusions obtained from spectroscopic data. The use of toluene hydrogenation and ethanol decomposition as test reactions provides useful information on the state of the surface of palladium–copper bi-metallic catalysts. The results of the catalytic tests are consistent with what is expected from the various methods of preparation selected in this study.

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